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(21) International Application Number: PCT/US88/04176 (22) International Filing Date: 23 November 1988 (23.11.88) (31) Priority Application Number: 124,718 (32) Priority Date: 24 November 1987 (24.11.87) (33) Priority Country: US (71) Applicant: PPG INDUSTRIES, INC. [US/US]; One PPG Place, Pittsburgh, PA 15272 (US). (72) Inventors: HAYNES, Ronald, L. ; 518 Wilson Avenue, Barberton, OH 44203 (US). HOELSCHER, Charles, H. ; 16290 Old Chippewa Trail, Doylestown, OH 44230 (US). LASCH, Jonathan, G. ; 750 Mull Avenue, Apt. 7B, Akron, OH 44313 (US).		(74) Agents: STEIN, Irwin, M.; PPG Industries, Inc., One PPG Place, Pittsburgh, PA 15272 (US) et al. (81) Designated States: CH (European patent), DE (European patent), GB (European patent), IT (European patent), JP. Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: ORGANIC PHOTOCHROMIC PIGMENT (57) Abstract <p>Described is photochromic particulate material comprising a photochromic substance within a matrix of a polymerizate of a polyfunctional acrylate monomer and a method of making the photochromic substance. The photochromic material may be produced by adding an organic photochromic substance to a polymerizable composition including a polyfunctional acrylate monomer and polymerizing the resultant admixture, e.g., by emulsion polymerization. The particulate material is useful in making glass and plastic composites that have a photochromic response.</p>		

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ORGANIC PHOTOCHROMIC PIGMENT

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DESCRIPTION OF THE INVENTION

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The present invention relates to novel organic photochromic materials, to methods for preparing such materials and to compositions and articles containing same. The terms "photochromic substance" or "photochromic material", as used herein, is intended to mean and include a substance, material, compound or composition which changes its optical transmission or reflectance when subjected to ultraviolet or visible light and which subsequently reverts to its original color or hue upon removal of that light source. A photochromic article is an article containing a photochromic substance or material.

Photochromic compounds, such as spiro(indoline) benzopyrans, spiro(indoline) naphthoxazines and spiro(indoline) pyridobenzoxazines are known in the art. See, for example, U.S. patents 4,342,668 and 4,637,698. By and large, the methods used for incorporating such photochromic compounds within an organic plastic host has involved incorporating the photochromic compound into the already polymerized host. This is so because polymerization of monomer compositions producing the polymeric host generally requires use of initiators of the peroxide or peroxy ester type. Such initiators are oxidizing agents and are believed to nullify the photochromic behavior of the photochromic compound, probably by oxidation of a portion of the photochromic compound's structure.

Methods used to incorporate photochromic compounds into an organic plastic host include surface dyeing, dissolving the optically transparent resin and photochromic compound in a mutual solvent and using the solution to coat a previously shaped article, e.g., a lens,

1 plate, sheet, film or fiber; dissolving the photochromic compound
into a liquid optically transparent resin and casting the resin in
3 the form of a film or sheet, and by imbibition, i.e., by diffusion of
the photochromic compound into the preformed plastic host material by
5 a suitable transfer mechanism such as thermal or vapor phase
transfer. See, for example, U.S. patents 3,216,958 and 4,637,698,
7 and European patent application 171,909.

U.S. patent 3,565,814 suggests that benzospiropyran
9 compounds may be incorporated into a lauryl methacrylate polymer by
incorporating the benzospiropyran into lauryl methacrylate monomer
11 and polymerizing the monomer with peroxy-type initiators. Recently
there has been proposed a direct casting process for manufacturing a
13 shaped synthetic plastic article having photochromic properties by
incorporating a photochromic spiro-oxazine compound into a mixture
15 containing a highly reactive polyfunctional monomer and a low level
of a polymerization catalyst, and casting the resultant composition
17 in a mold to form the shaped synthetic plastic article. See European
patent application 227,337. It has also been suggested in U.S.
19 patent 4,012,232 that crystals of photochromic compounds be coated
with inorganic oxides to place a protective coating of the inorganic
21 oxide around the crystal. Such coated crystals may be dispersed in
polymerizable monomers and the resultant mixture polymerized.

23 It has now been discovered the the property of photochromism
can be extended to many different applications and monomer systems by
25 use of the organic photochromic pigments of the present invention.

More particularly, it has been discovered that an organic
27 photochromic substance, such as spiro(indoline)-type compounds, may
be incorporated into thermoset materials and a particulate form of
29 that material used in any application where pigmentary materials are
used. In accordance with the present invention, an organic
31 photochromic substance or composition is admixed uniformly with a
polymerizable monomeric composition including a polyfunctional
33 acrylate monomer and the resulting mixture polymerized, e.g., by
emulsion polymerization, to produce finely-divided thermoset

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1 photochromic material having the photochromic substance or
 composition substantially uniformly dispersed throughout the product,
 3 e.g., the finely divided particles prepared by emulsion
 polymerization.

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DETAILED DESCRIPTION OF THE INVENTION

7

Polyfunctional acrylate monomers that may be used to prepare
 9 the thermoset photochromic particles described herein are
 esterification products of an acrylic acid moiety selected from the
 11 group consisting of acrylic acid and methacrylic acid, and a polyol,
 e.g., a diol, a triol or tetracarbinol. More particularly, the
 13 polyfunctional acrylate monomer may be represented by the following
 graphic formula I:

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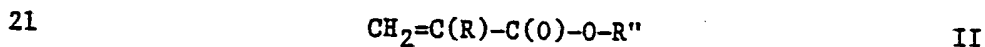
wherein R is hydrogen or methyl, n is the number 2, 3, or 4, and R'
 19 is the multivalent radical, i.e., a bivalent, trivalent or
 quadravalent radical, remaining after removal of the hydroxy groups
 21 from a polyol, having from 2 to 4 hydroxy groups, e.g., a diol, triol
 or tetracarbinol respectively. More particularly, R is hydrogen or
 23 methyl, and n is 2 or 3, more usually 2.

R' may be selected from the group consisting of alpha, omega
 25 C₂-C₈ glycols, cyclohexane diol, diethylene glycol, triethylene
 glycol, tetraethylene glycol, dipropylene glycol, C₂-C₅ triols and
 27 pentaerythritol. Examples of such polyols include ethylene glycol,
 trimethylene glycol, 1,4-butane diol, 1,5-pentane diol, 1,6-hexane
 29 diol, propylene glycol, trimethylol propane, glycerol and the like.

Examples of polyfunctional acrylate monomers, such as
 31 diacrylates and triacrylates, include: ethylene glycol diacrylate,
 ethylene glycol dimethacrylate, 1,2-propane diol diacrylate,
 33 1,3-propane diol diacrylate, 1,2-propane diol dimethacrylate,
 1,3-propane diol dimethacrylate, 1,4-butane diol diacrylate,

1 1,3-butane diol dimethacrylate, 1,4-butane diol dimethacrylate,
 2 1,5-pentane diol diacrylate, 2,5-dimethyl-1,6-hexane diol
 3 dimethacrylate, diethylene glycol diacrylate, diethylene glycol
 4 dimethacrylate, triethylene glycol dimethacrylate, trimethylol
 5 propane trimethacrylate, tetraethylene glycol diacrylate,
 6 tetraethylene glycol dimethacrylate, dipropylene glycol diacrylate,
 7 dipropylene glycol dimethacrylate, trimethylol propane triacrylate,
 8 glycerol triacrylate, glycerol trimethacrylate, pentaerythritol
 9 triacrylate, pentaerythritol dimethacrylate, pentaerythritol
 10 tetraacrylate, pentaerythritol tetramethacrylate and mixtures of such
 11 acrylate monomers.

A portion of the polyfunctional acrylate monomer may be
 13 replaced with a monofunctional copolymerizable monomer containing the
 14 vinyl ($\text{CH}_2=\text{CH}-$) grouping. Such compatible monomers include
 15 monofunctional acrylic and methacrylic acid esters, and vinyl esters
 16 of $\text{C}_2\text{-C}_6$ carboxylic acids, i.e., vinyl carboxylates. Preferably, the
 17 copolymerizable monomer is a non-aromatic, e.g., non-benzenoid,
 18 containing monomer. Monofunctional acrylic or methacrylic ester
 19 monomers may be graphically illustrated by the following formula,



23 wherein R is hydrogen or methyl, and R'' is selected from the group
 24 consisting of $\text{C}_1\text{-C}_{12}$, e.g., $\text{C}_1\text{-C}_8$, alkyl, $\text{C}_5\text{-C}_6$ cycloalkyl, glycidyl
 25 and hydroxyethyl. Preferably, R'' is a $\text{C}_1\text{-C}_4$ alkyl, e.g., methyl, or
 26 cyclohexyl.

27 Examples of monofunctional acrylic acid type monomers
 28 include, for example, the acrylic and methacrylic acid esters of
 29 alkanols such as methanol, ethanol, propanol, butanol, pentanol,
 30 hexanol, heptanol and octanol, e.g., methyl acrylate, methyl
 31 methacrylate, ethyl acrylate and ethyl methacrylate, cycloalkanols
 32 such as cyclopentanol and cyclohexanol, glycidol (3-hydroxy propylene
 33 oxide, (d, l, dl)) and ethylene glycol. Examples of vinyl
 34 carboxylates include vinyl acetate, vinyl propionate, vinyl butyrate
 35 and vinyl valerate. In addition to and/or in place of the

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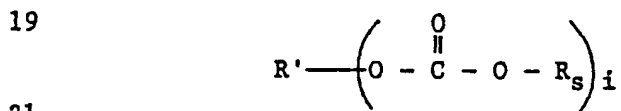
1 aforescribed monofunctional copolymerizable monomer, monofunctional
allylic and difunctional allylic copolymerizable compatible monomers
3 may also replace a portion of the polyfunctional acrylate monomer.

Monofunctional allylic monomers contemplated include allyl esters of
5 C₂-C₆ carboxylic acids, C₁-C₆ allyl ethers and other copolymerizable
allyl compounds. Preferably the monofunctional allylic monomer is a
7 non-aromatic compound.

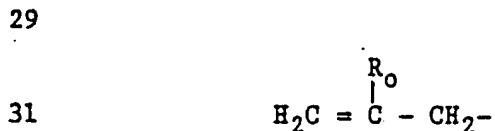
Difunctional allylic copolymerizable monomers contemplated
9 herein are polyol (allyl carbonates) such as the allyl carbonates of
linear or branched aliphatic or aromatic liquid polyols, e.g.,
11 aliphatic glycol bis(allyl carbonate) compounds, or alkylidene
bisphenol bis(allyl carbonate) compounds. These monomers can be
13 described as unsaturated polycarbonates of polyols, e.g., glycols.

The monomers can be prepared by procedures well known in the art,
15 e.g., U.S. Patents 2,370,567 and 2,403,113.

The polyol (allyl carbonate) monomers can be represented by
17 the graphic formula:



wherein R_s is the radical derived from an allyl or substituted allyl
23 group, R'_s is the radical derived from the polyol, and i is a whole
number from 2 - 5, preferably 2. The allyl group (R_s) can be
25 substituted at the 2 position with a halogen, most notably chlorine
or bromine, or an alkyl group containing from 1 to 4 carbon atoms,
27 generally a methyl or ethyl group. The R_s group can be represented
by the graphic formula:

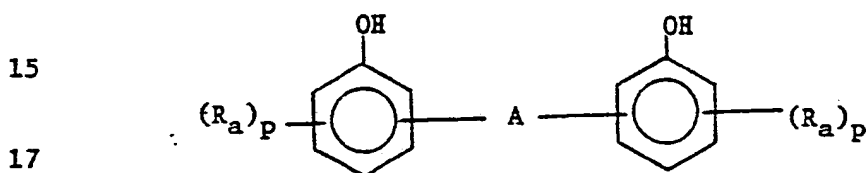


33 wherein R₀ is hydrogen, halogen, or a C₁-C₄ alkyl group. Specific
examples of R_s include the groups: allyl, 2-chloroallyl,
35 2-bromoallyl, 2-fluoroallyl, 2-methallyl, 2-ethylallyl,

1 2-isopropylallyl, 2-n-propylallyl, and 2-n-butylallyl. Most commonly
 3 R_s is the allyl group, $H_2C = CH - CH_2-$.

3 R'_s is a polyvalent radical derived from the polyol, which
 can be an aliphatic or aromatic polyol that contains 2, 3, 4 or 5
 5 hydroxy groups. Typically, the polyol contains 2 hydroxy groups,
 i.e., a glycol or bisphenol. The aliphatic polyol can be linear or
 7 branched and contain from 2 to 10 carbon atoms. Commonly, the
 aliphatic polyol is an alkylene glycol having from 2 to 4 carbon
 9 atoms or a poly(C_2-C_4) alkylene glycol, i.e., ethylene glycol,
 propylene glycol, trimethylene glycol, tetramethylene glycol, or
 11 diethylene glycol, triethylene glycol, etc.

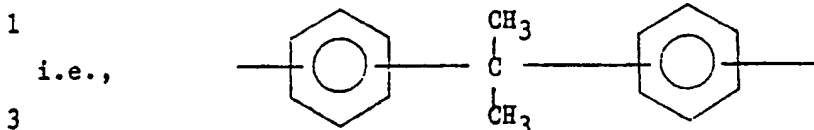
The aromatic polyol can be represented by the graphic
 13 formula:



19 wherein A is a bivalent radical derived from an acyclic aliphatic
 hydrocarbon, e.g., an alkylene or alkylidene radical, having from 1
 21 to 4 carbon atoms, e.g., methylene, ethylene, and dimethylmethylene
 (isopropylidene:), R_a represents lower alkyl substituents of from 1
 23 to 3 carbon atoms, and p is 0, 1, 2, or 3. Preferably, the hydroxyl
 group is in the ortho or para position.

25 Specific examples of the radical R'_s include: alkylene
 groups containing from 2 to 10 carbon atoms such as ethylene,
 27 $(-CH_2-CH_2-)$, trimethylene, methylethylene, tetramethylene,
 ethylethylene, pentamethylene, hexamethylene, 2-methylhexamethylene,
 29 octamethylene, and decamethylene; alkylene ether groups such as
 $-CH_2-O-CH_2-$, $-CH_2CH_2-O-CH_2CH_2-$, $-CH_2-O-CH_2-CH_2-$, and
 31 $-CH_2CH_2CH_2-O-CH_2CH_2CH_2-$; alkylene polyether groups such as
 $-CH_2CH_2-O-CH_2CH_2-O-CH_2CH_2-$, and $-CH_2CH_2CH_2-O-CH_2CH_2CH_2-O-CH_2CH_2CH_2-$;
 33 alkylene carbonate and alkylene ether carbonate groups such as
 $-CH_2CH_2-O-CO-O-CH_2CH_2-$ and $-CH_2CH_2-O-CH_2CH_2-O-CO-O-CH_2CH_2-O-$
 35 CH_2CH_2- ; and isopropylidene bis(para-phenyl),

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5 Most commonly, R'_S is $-\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-$, or
 $-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-$.

7 Specific examples of polyol (allyl carbonate) monomers
 include ethylene glycol bis(2-chloroallyl carbonate), ethylene glycol
 9 bis(allyl carbonate), diethylene glycol bis(2-methallyl carbonate),
 diethylene glycol bis(allyl carbonate), triethylene glycol bis(allyl
 11 carbonate), propylene glycol bis(2-ethylallyl carbonate),
 1,3-propanediol bis(allyl carbonate), 1,3-butanediol bis(allyl
 13 carbonate), 1,4-butanediol bis(2-bromoallyl carbonate), dipropylene
 glycol bis(allyl carbonate), trimethylene glycol bis(2-ethylallyl
 15 carbonate), pentamethylene glycol bis(allyl carbonate), and
 isopropylidene bisphenol bis(allyl carbonate).

17 In addition, a partially polymerized form of the polyol
 (allyl carbonate) monomer can be used. In that embodiment, the
 19 monomer is thickened by heating or partially polymerized by using
 small, e.g., 0.5-1.5 parts of initiator per hundred parts of monomer
 21 (phm), to provide a non-gel containing, more viscous monomeric
 material.

23 As used in the present description and claims, the term
 polyol(allyl carbonate) monomer or like names, e.g., diethylene
 25 glycol bis(allyl carbonate), are intended to mean and include the
 named monomer or prepolymer and any related monomer species contained
 27 therein.

The amount of polyfunctional acrylate monomer that may be
 29 replaced with copolymerizable (monofunctional and/or difunctional
 vinylic or allylic) monomer is generally less than 50, e.g., less
 31 than 20 weight percent. Such amounts may vary from about 1 to about
 20 weight percent. Thus, the polyfunctional acrylate monomer
 33 composition may contain from about 0 to about 20 weight percent of
 copolymerizable monomer.

35 The polymer product (resin) resulting from polymerization of

1 the polyfunctional acrylate monomer composition is a thermoset
2 material. As used herein the term polyfunctional acrylate monomer
3 composition is intended to mean and include a polymerizable
4 composition containing polyfunctional acrylate monomer alone or
5 together with components selected from the group consisting of
6 copolymerizable compatible monomer (monofunctional and/or
7 difunctional) and adjuvants such as ultraviolet light absorbers,
8 antioxidants, stabilizers, etc. By "thermoset" is meant that upon
9 complete polymerization of the monomer composition, the resulting
10 resin is infusible and substantially insoluble in nearly all
11 solvents. Further application of heat, short of that which will char
12 or disintegrate the resin, will produce no appreciable changes
13 therein. The thermoset resin should be relatively brittle to allow
14 it to be ground into finely divided particles, but the resin has a
15 high degree of physical and chemical integrity, i.e., it is resistant
16 to the action of common bases, acids and detergents, and is insoluble
17 in common organic solvents. The polyfunctional acrylate monomer(s)
18 and copolymerizable monomer (if used) are selected so that the
19 resultant polymerizate is highly cross-linked and, therefore,
20 relatively brittle, i.e., it can be ground or milled readily to
21 reduce its size to a pigmentary size range (as described herein)
22 using conventional attrition milling devices, e.g., ball mills.

23 The polymer product will usually be transparent, but may be
24 translucent or even opaque. The polymer product need only be
25 transparent to that portion of the electromagnetic spectrum, which
26 activates the photochromic compound, i.e., that wavelength of
27 ultraviolet light that produces the open form of the compound and
28 that portion of the visible spectrum that includes the absorption
29 maxima wavelength of the compound in its UV activated form, i.e., the
30 open form. Further, the resin color should not be such that it masks
31 the color of the activated form of the photochromic compound, i.e.,
32 so the change in color is readily apparent to the observer.

33 Polymerization of the polyfunctional acrylate monomer
34 composition may be performed using conventional polymerization
35 techniques that are used for acrylate-type monomers. The

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1 polymerization may be performed in bulk or by a suspension or
emulsion process. A considerable body of literature concerned with
3 the polymerization of acrylic ester monomers has been developed and
such literature may be used to perform the polymerizations described
5 herein. The exact polymerization process used will be governed by
the physical form of the particulate photochromic material desired
7 and by the photochromic substance which is to be incorporated into
such particulate product. For example, a polymerization process
9 should be used which does not utilize procedures or materials that
will interfere with the photochromic substance and thereby nullify
11 the reversible color changeability of that substance, i.e., if a
particular polymerization process requires the use of ingredients to
13 which the photochromic substance is sensitive, then a different
process should be utilized. The same is true of polymerization
15 processes requiring conditions of high temperature, solvent,
catalyst, etc.

17 Bulk polymerization may be used to continuously cast sheets
of the polymer product or to produce sheets in molds by a batch
19 process. Such sheets may be granulated and then ground into
particles of the desired size. The bulk polymerization process is
21 difficult to control due to the need remove heat from the
polymerization media and is, therefore, not the preferred
23 polymerization process to be used.

In suspension polymerization, the monomer composition is
25 suspended in water as 0.1 to about 5 millimeter (mm) droplets, which
are stabilized by protective colloids or suspending agents.
27 Polymerization is initiated by a monomer-soluble initiator and takes
place within the monomer droplets. The suspending medium, i.e.,
29 water, serves as both the dispersing medium and as a heat transfer
agent. Particle size is controlled primarily by the rate of
31 agitation and the concentration and type of suspending aids
utilized. The polymer product is obtained as small beads of about
33 0.1 to about 5 mm in diameter, which may be isolated by filtration or
centrifugation.

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1 Suitable protective colloids used in suspension
polymerization include cellulose derivatives, polyacrylate salts,
3 starch, poly(vinyl alcohol), gelatin, talc, clay and clay
derivatives. These ingredients prevent the monomer droplets from
5 coalescing during polymerization.

 Initiators that may be used for bulk or suspension
7 polymerization of acrylate monomers include peroxides,
hydroperoxides, peresters, percarbonates, and azo-type catalysts.
9 Examples of such initiators include methyl ethyl ketone peroxide,
benzoyl peroxide, cumene hydroperoxide, tertiarybutyl peroctoate,
11 diisopropyl peroxydicarbonate, dicyclohexyl peroxydicarbonate,
tertiarybutylperoxy isopropylcarbonate, lauroyl peroxide and
13 2,2'-azobisisobutyronitrile.

 Emulsion polymerization of the polyfunctional acrylate
15 monomer composition provides a convenient method for the preparation
of high solids, low viscosity latices. Emulsion polymerization
17 utilizes a relatively large amount, e.g., 1-5 weight percent, of
nonionic or anionic surfactants to emulsify the monomer composition.
19 In an emulsion polymerization, product particle size is controlled by
the concentration and type of emulsifier used. Anionic soaps usually
21 produce finer particles. Further, blends of emulsifiers are often
used. Sodium lauryl sulfate is a common anionic surfactant that is
23 used for such polymerizations.

 Typically, a water soluble initiator or a redox initiator
25 system is used to initiate the emulsion polymerization. Persulfates,
such as potassium persulfate, ammonium persulfate or sodium
27 persulfate, or hydrogen peroxide are typically used as the
water-soluble initiator. Other initiators that may be used include
29 organic peroxygen compounds such as tertiarybutyl hydroperoxide,
cumene hydroperoxide, lauroyl peroxide, benzoyl peroxide and methyl
31 ethyl ketone peroxide. In the case of a redox initiating system, a
peroxygen compound such as a persulfate or organic hydroperoxide and
33 a reducing agent such as sodium bisulfite, sodium sulfite, sodium
metabisulfate, sodium thiosulfate, sodium hydrosulfite and sodium
35 formaldehyde sulfoxylate are used, often with a small amount of

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1 ferrous sulfate activator. Typically, 1 part of the peroxygen
compound, 0.1-1.5 parts of the reducing agent and 0.001-0.002 parts
3 of a water soluble metal salt are used, e.g., a
persulfate-bisulfite-ferrous sulfate redox initiator system.

5 In performing an emulsion polymerization, the monomer is
emulsified by adding the emulsifier and monomer(s) to deionized water
7 with good agitation. The initiator system is then added to the
emulsified monomer and, after a brief induction period, the
9 polymerization reaction begins with a vigorous rise in temperature.
Alternatively, the initiator may be added to a reactor containing
11 deionized water and emulsifier, e.g., sodium lauryl sulfate, and
thereafter emulsified monomer introduced slowly to the reactor. The
13 polymerized product is cooled to room temperature and recovered by
filtration or other suitable solid-liquid separating means.

15 The particulate thermoset polymeric product useful as the
organic photochromic pigment described herein will preferably have an
17 average particle size diameter in the range of between about 0.25 and
about 20 micrometers, more particularly, 0.25-5 micrometers, e.g., 1
19 to 2 micrometers. In some applications, it is preferred that the
particle size range between about 0.25 and about 1 micrometer. Such
21 particle sizes may be obtained by controlling the conditions of the
suspension and emulsion polymerization process using techniques known
23 in the art, e.g., by regulating the size of dispersed monomer
droplets in suspension polymerization and by selecting the amount of
25 surfactant which will yield the desired particle size in emulsion
polymerization. In the case of bulk polymerization where the product
27 may be a cast thin sheet, particles of the desired size may be
obtained by granulating and grinding the sheet with conventional
29 pulverizing equipment such as hammer mills, rod mills, ball mills,
roller mills, fluid energy mills, micronizers and other type of
31 attrition milling equipment. Particulate product prepared by
emulsion or suspension polymerization methods may also be reduced in
33 average particle size, if desired, by utilization of the
aforedescribed milling apparatus. This may occur when the

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1 polymerization process yields a spheroidal particulate product larger
in average particle diameter than desired for a particular
3 application.

Wet milling methods are not recommended as that method may
5 leach the photochromic substance from the particles being ground.
Dry milling or grinding is preferred. During dry grinding, it is
7 recommended that the particles be kept relatively cool. This may be
achieved by providing external cooling to the pulverizing equipment
9 or by periodically halting the milling process to allow the particles
to cool. Moreover, rinsing or washing the particles with a solvent
11 such as methanol may extract some of the photochromic substance from
the particles.

13 In preparing the photochromic particulate thermoset
materials of the present invention, at least one organic photochromic
15 substance is dissolved or dispersed in the polyfunctional acrylic
monomer composition to be polymerized. This may be accomplished by
17 physically mixing the monomer composition with the photochromic
substance with sufficient agitation to accomplish the dissolution or
19 dispersion with or without mild heating to enhance the rate of
dissolution. The amount of photochromic substance(s) incorporated
21 into the monomeric composition may vary and will depend on the
photochromic substance's solubility in the monomer composition.
23 Typically, a sufficient amount of the photochromic substance is added
to the monomer composition so that the resulting particulate resin
25 (polymerizate) is photochromic, i.e., produces a photochromic effect.

By "photochromic" or "photochromic effect" is meant that
27 when the particulate resin is exposed to ultraviolet light, the
particles visibly change color (or become colored) and then return to
29 their original color or colorless state when the ultraviolet light is
removed. The photochromic effect may be readily observed by exposing
31 the particulate resin containing the photochromic substance to a
source of ultraviolet light such as the sun or to an artificial
33 ultraviolet light source such as a Spectroline® lamp, Model
ENF-28(365) nanometers.

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1 The amount of photochromic substance(s) incorporated within
the particulate resin may vary greatly. The lower limit is that
3 amount which will still provide a photochromic effect, while the
upper limit is defined by the solubility of the photochromic
5 substance in the monomer and resulting resin. Generally, the amount
of photochromic substance(s) incorporated into the polymerizable
7 polyfunctional acrylate composition or particulate resin may vary
from about 0.01 to about 10 weight percent. When the particulate
9 resin is used directly, i.e., without dilution with other
non-photochromic resin, the amount of photochromic substance(s)
11 incorporated therein will usually range from about 0.01 to about 2
weight percent, more particularly from about 0.01 to about 1 weight
13 percent, e.g., from about 0.1 or 0.5 to about 1 weight percent.

In another embodiment, it is contemplated that photochromic
15 particulate resin is prepared containing higher amounts of
photochromic substance(s), e.g., up to the solubility limit of the
17 photochromic substance(s) in the resin. This resin is used as a
concentrate and is subsequently diluted or let down with
19 non-photochromic resin prior to use. In preparing such concentrates,
it is contemplated that the amount of photochromic substance(s) in
21 the resin will vary from about 2 to about 10 weight percent, e.g.,
from about 5 to about 10 weight percent. The greater the amount of
23 photochromic compound incorporated into the particulate resin, the
greater the intensity of the color of the particles upon irradiation.

25 Photochromic substances contemplated for use in preparing
the organic photochromic pigment of the present invention are organic
27 substances, including spiro(indoline)-type compounds, that provide a
visual photochromic response when incorporated into the particulate
29 resin described hereinabove, that are dispersible, e.g., soluble,
within the polyfunctional acrylate monomeric composition and that are
31 chemically compatible with such monomeric composition and the
resulting resin polymerizate.

33 Particularly contemplated photochromic substances include
spiro(indoline)-type compounds, such as spiro(indoline)

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1 pyridobenzoxazines, spiro(indoline) naphthoxazines,
 2 spiro(benzindoline), pyrido benzoxazines, spiro(benzindoline)
 3 naphthoxazines, spiro(indoline) benzopyrans, spiro(indoline)
 4 naphthopyrans, spiro(indoline) quinopyrans, spiro(indoline)
 5 benzoxazines, and metal dithizonate compounds, fulgides or
 6 fulgimides, and spiro(di)hydroindolizines. The particular
 7 photochromic substance selected for use will depend on its
 8 compatibility with the monomeric composition and particulate resin
 9 product, including its solubility therein, and the particular change
 10 in color exhibited by the photochromic substance when incorporated
 11 into the particulate resin product and irradiated with ultraviolet
 12 light. Particularly contemplated are the spiro(indoline)-type
 13 compounds, such as spiro(indoline) naphthoxazines and spiro(indoline)
 14 pyridobenzoxazines.

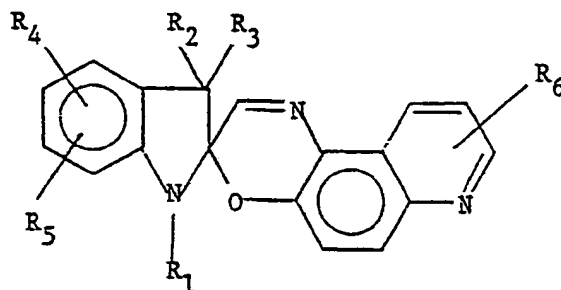
15 Spiro(indoline)pyrido benzoxazines contemplated herein may
 16 be represented by the following graphic formula:

17

19

21

23



III

24 In the above graphic formula III, R_1 is selected from the group
 25 consisting of C_1 - C_8 alkyl, e.g., methyl, ethyl, propyl, butyl, etc.,
 26 phenyl, phen(C_1 - C_4) alkyl, e.g., benzyl, naphth (C_1 - C_4) alkyl, e.g.,
 27 1-naphthylmethyl, allyl, acrylyl, methacrylyl, carboxy (C_2 - C_6) alkyl,
 28 e.g., β -carboxyethyl, γ -carboxypropyl and δ -carboxybutyl, cyano
 29 (C_2 - C_6) alkyl, e.g., β -cyanoethyl, γ -cyanopropyl,
 30 β -cyanoisopropyl, and δ -cyanobutyl, C_1 - C_4 acyloxy (C_2 - C_6) alkyl,
 31 i.e., $[R_cC(O)R_d-]$, where R_c is a C_1 - C_4 alkyl and R_d is a C_2 - C_6 alkyl],
 32 e.g., acetoxyethyl, acetoxypropyl, propionyloxyethyl, acetoxybutyl,
 33 and propionyloxypropyl, hydroxy (C_2 - C_6) alkyl, e.g., hydroxyethyl,
 34 hydroxypropyl and hydroxybutyl, $(C_2H_4O)_m \cdot CH_3$, wherein m is a number
 35 from 1 to 6, and mono- and di-substituted phenyl, said phenyl

1 substituents being selected from C_1-C_4 alkyl and C_1-C_5 alkoxy, e.g.,
methoxy, ethoxy, propoxy, butoxy and pentoxy. Preferably, R_1 is
3 selected from the group consisting of a C_1-C_4 alkyl, phenyl, benzyl,
1-naphth (C_1-C_2) alkyl, carboxy (C_2-C_4) alkyl, cyano (C_2-C_4) alkyl,
5 C_1-C_4 acyloxy (C_2-C_4) alkyl, e.g., C_1-C_4 -acyloxyethyl, hydroxy
(C_2-C_4) alkyl and $(C_2H_4O)_m \cdot CH_2$, wherein m is a number of from 1 to
7 3, e.g., 2.

R_2 and R_3 of formula III are each selected from the group
9 consisting of C_1-C_5 alkyl, phenyl, mono- and di-substituted phenyl,
benzyl or R_2 and R_3 may combine to form a cyclic ring selected from
11 the group consisting of an alicyclic ring containing from 6 to 8
carbon atoms (including the spiro carbon atom), norbornyl and
13 adamantyl. The aforesaid phenyl substituents may be selected from
 C_1-C_4 alkyl and C_1-C_5 alkoxy radicals. More particularly, R_2 and R_3
15 are each selected from C_1-C_5 alkyl, e.g., methyl, ethyl, propyl,
butyl and pentyl, and phenyl. When one of R_2 or R_3 is a tertiary
17 alkyl radical, such as tertiary butyl or tertiary amyl, the other is
preferably an alkyl radical other than a tertiary alkyl radical.

19 R_4 and R_5 in graphic formula III are each selected from the
group consisting of hydrogen, C_1-C_5 alkyl, halogen, e.g., chloro and
21 fluoro, C_1-C_5 alkoxy, nitro, cyano, C_1-C_4 monohaloalkyl, e.g.,
chloromethyl, fluoromethyl, chloroethyl, chloropropyl, etc., C_1-C_4
23 polyhaloalkyl, e.g., trihaloalkyl, C_1-C_8 alkoxy carbonyl, and C_1-C_4
acyloxy, i.e., $R_cC(O)-$, wherein R_c is a C_1-C_4 alkyl, such as
25 acetoxy. While any halogen, i.e., chlorine, bromine, iodine and
fluorine, may be used in respect to the halogen or haloalkyl
27 substituents, chlorine, fluorine and bromine, especially chlorine and
fluorine is preferred for the halogen substituent and fluorine is
29 preferred for the polyhaloalkyl substituent, e.g., trifluoromethyl
(CF_3). Preferably, R_4 and R_5 are each selected from the group
31 consisting of C_1-C_2 alkyl, e.g., methyl and ethyl, chlorine,
fluorine, C_1-C_2 trihaloalkyl, e.g., trihalomethyl such as
33 trifluoromethyl, and C_1-C_5 alkoxy, e.g., methoxy and ethoxy. R_4 and
 R_5 may be located on any two of the available carbon atoms of the
35 indolino portion of the compound, i.e., on the 4, 5, 6 or 7

- 16 -

1 positions. Preferably, when the substituents are other than
hydrogen, they are located at the 4 and 5, 5 and 6, 4 and 7 or 6 and
3 7 positions.

It is possible that the spiro(indoline) pyrido benzoxazines
5 of graphic formula III can be a mixture of isomers due to the
alternative directional mechanisms by which intramolecular
7 condensation occurs during formation of the starting indol reactant
(Fischer's base). Indolization of 3-substituted phenylhydrazones can
9 give rise to a 4-substituted indole, a 6-substituted indole, or
mixtures thereof. When R_4 and R_5 are both other than hydrogen,
11 substitution on the benz portion of the indolino ring may comprise an
isomeric mixture, e.g., a mixture of substituents at the 4 and 5, 4
13 and 5, 5 and 6, 4 and 7, 5 and 7 and 6 and 7 positions. Commonly,
such substituents are located at the 4 and 5 or 5 and 6 positions,
15 and thus there may be an isomeric mixture of such substituents, e.g.,
4 (and 6) and 5- substituted compounds.

17 R_6 in graphic formula III may be selected from the group
consisting of hydrogen, C_1 - C_5 alkyl, e.g., C_1 - C_2 alkyl, C_1 - C_5 alkoxy,
19 e.g., C_1 - C_2 alkoxy, and halogen, e.g., chloro, fluoro or bromo.
Preferably, R_6 is hydrogen.

21 Of particular interest, are spiro(indoline)pyrido
benzoxazines represented by graphic formula III wherein R_1 is a C_1 - C_4
23 alkyl, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, secondary
butyl, isobutyl and tertiary butyl; R_2 and R_3 are each methyl, ethyl
25 or phenyl; and R_4 and R_5 are each methyl, methoxy, trifluoromethyl,
chloro or fluoro.

27 The spiro(indoline)pyrido benzoxazines described above can
be synthesized by reaction of the corresponding nitroso-hydroxy
29 quinoline compound with the corresponding free indoline (Fischer's
base) or indolium salt, e.g., the iodide salt, compound. The two
31 precursor materials are refluxed in a suitable solvent such as
toluene or isopropanol until the reaction is completed. A base, such
33 as triethylamine, is present in the reaction medium when the indolium
salt is used as the reactant. See, for example, U.S. Patent
35 4,637,698, which describes the aforesaid spiro(indoline) pyrido

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1 benzoxazines and their synthesis. The aforesaid patent is
incorporated herein by reference.

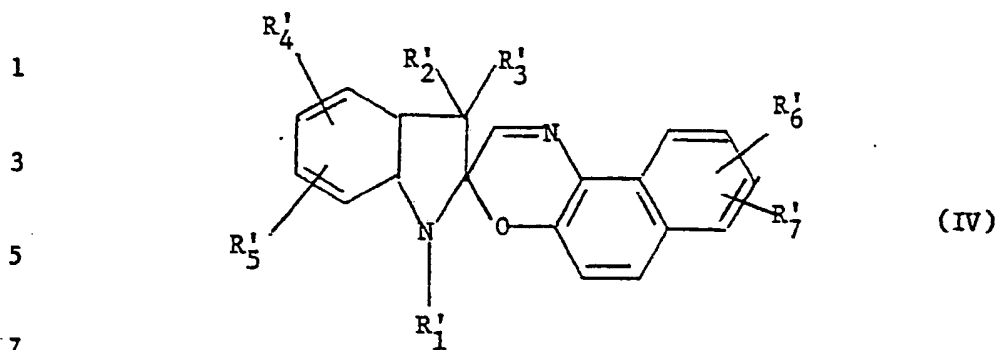
3 Examples of spiro(indoline)pyrido benzoxazines that may be
used in the practice of the present invention include those in Table
5 I wherein R_1 , R_2 , R_3 , R_4 and R_5 are as listed and R_6 is hydrogen.

7 Table I

9 Compound	R_1	R_2	R_3	R_4	R_5
11					
1	CH ₃	CH ₃	CH ₃	H	H
13 2	CH ₃	CH ₃	CH ₃	CH ₃	CH ₃
3	CH ₃	CH ₃	CH ₃	OCH ₃	H
15 4	CH ₃	CH ₃	CH ₃	Cl	CH ₃
5	CH ₃	CH ₃	C ₂ H ₅	H	H
17 6	CH ₃	CH ₃	C ₂ H ₅	CH ₃	CH ₃
7	CH ₃	C ₂ H ₅	C ₂ H ₅	H	H
19 8	n-C ₄ H ₉	CH ₃	C ₂ H ₅	H	H
9	CH ₃	CH ₃	phenyl	H	H
21 10	CH ₃	phenyl	phenyl	H	H
11	C ₂ H ₅	CH ₃	C ₂ H ₅	CH ₃	CH ₃
23 12	n-C ₄ H ₉	CH ₃	C ₂ H ₅	CH ₃	CH ₃

25 Compound 2 in Table I may be named 1,3,3,4,5-(or 1,3,3,5,6-)
pentamethylspiro [indoline-2,3' [3H] pyrido [3,2-f] [1,4]
27 benzoxazine]. Similarly, compound 6 in Table I may be named
1,3,5,6-tetramethyl-3-ethylspiro [indoline-2,3' [3H] pyrido [3,2-f]
29 [1,4] benzoxazine]. Other compounds in Table I can be similarly
named taking into account the different substituents.

31 Spiro(indoline)naphthoxazines contemplated herein may be
represented by the following graphic formula:



Spiro(indoline)naphthoxazines and their synthesis are described in, for example, U.S. Patents, 3,562,172, 3,578,602 and 4,215,010.

In graphic formula IV, R'_1 , R'_2 , R'_3 , R'_4 and R'_5 may be selected from those substituents described with respect to R_1 , R_2 , R_3 , R_4 and R_5 respectively in graphic formula III. R'_6 and R'_7 may each be selected from those substituents described with respect to R_6 in graphic formula III.

Examples of spiro(indoline)naphthoxazines contemplated herein, include those in which the substituents R'_1 - R'_7 are the following:

1

Table II

3	Compound	R ₁ '	R ₂ '	R ₃ '	R ₄ '	R ₅ '	R ₆ '	R ₇ '
5								
	1	CH ₃	CH ₃	CH ₃	H	H	OCH ₃	H
7	2	CH ₃	CH ₃	CH ₃	CH ₃	CH ₃	OCH ₃	H
	3	CH ₃	CH ₃	CH ₃	OCH ₃	H	OCH ₃	H
9	4	CH ₃	CH ₃	CH ₃	Cl	CH ₃	OCH ₃	H
	5	CH ₃	CH ₃	C ₂ H ₅	H	H	OCH ₃	H
11	6	CH ₃	CH ₃	C ₂ H ₅	CH ₃	CH ₃	OCH ₃	H
	7	CH ₃	C ₂ H ₅	C ₂ H ₅	H	H	OCH ₃	H
13	8	n-C ₄ H ₉	CH ₃	C ₂ H ₅	H	H	OCH ₃ H	
	9	CH ₃	CH ₃	phenyl	H	H	OCH ₃	H
15	10	CH ₃	phenyl	phenyl	H	H	OCH ₃	H
	11	CH ₃	p-C ₆ H ₄ OCH ₃	p-C ₆ H ₄ OCH ₃	H	H	OCH ₃ H	
17	12	C ₂ H ₅	CH ₃	C ₂ H ₅	CH ₃	CH ₃	OCH ₃	H
	13	n-C ₄ H ₉	CH ₃	C ₂ H ₅	CH ₃	CH ₃	OCH ₃ H	
19								

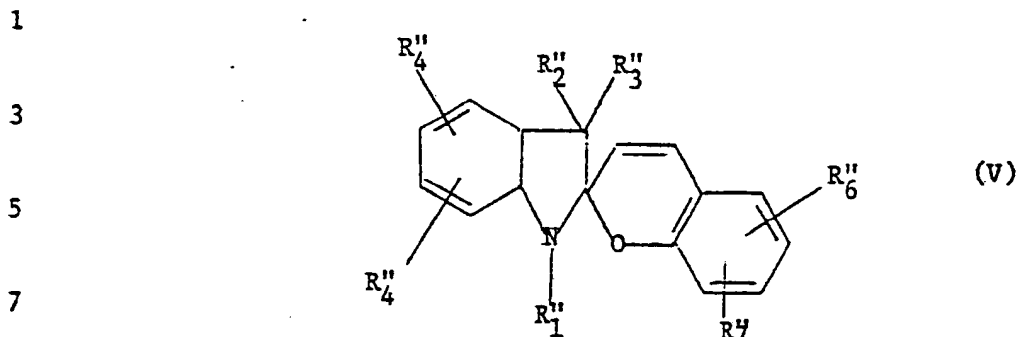
21 Compound 2 in Table II may be named 1,2,3,3,5,6-pentamethyl-9'-methoxyspiro[indolino-2,3' [3H] naphtho [2,1-b] [1,4]-oxazine].

23 Similarly, compound 6 in Table II may be named 1,3,5,6-tetramethyl-3-ethyl-9'-methoxyspiro [indolino-2,3' [3H]-naphtho [2,1-b]

25 [1,4]-oxazine]. Other compounds in Table II can be similarly named taking into account the different substituents.

27 Spiro(indoline)benzopyrans that are contemplated for use in the present invention include those represented by the following

29 graphic formula:



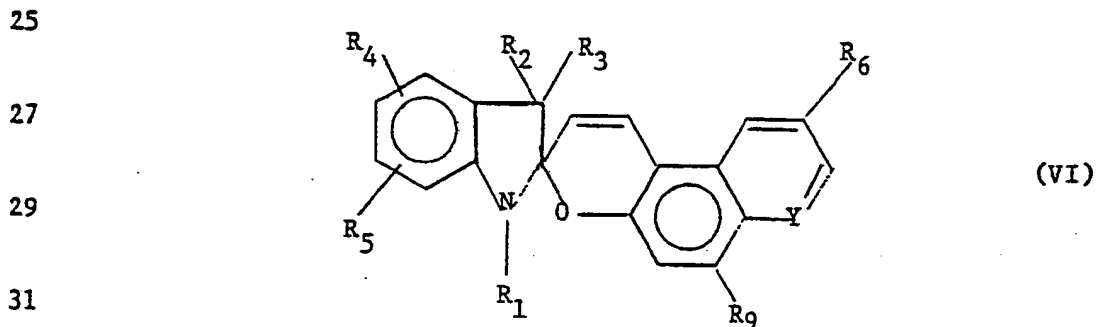
Spiro(indoline)benzopyrans are known in the art. These benzopyrans and their synthesis are described in U.S. Patent 3,100,778, 3,212,898 and 3,346,385 as well as in the British Patent 1,418,089.

In graphic formula V, R_1'' , R_2'' , R_3'' , R_4'' , R_5'' , R_6'' and R_7'' may be selected from those substituents described with respect to R_1' , R_2' , R_3' , R_4' , R_5' , R_6' and R_7' respectively in graphic formula IV, i.e., those substituents named with respect to R_1-R_6 in graphic formula III.

Examples of spiro(indoline)benzopyrans include:

1,3,3-trimethyl-6'-nitro-spiro(2H-1-benzopyran-2,2'-indoline); 1,3,3-trimethyl-6'-nitro-8'-methoxy-spiro(2H-1-benzopyran-2,2'-indoline); 1,3,3-trimethyl-6'-nitro-8'-bromo-spiro(2H-1-benzopyran-2,2'-indoline); 1,3,3-trimethyl-5'-bromo-6'-nitro-8'-methoxy-spiro(2H-1-benzopyran-2,2'-indoline); 1,3,3-trimethyl-5-chloro-6'-nitro-spiro(2H-1-benzopyran-2,2'-indoline); and 1-phenyl-3,3-dimethyl-6'-nitro-spiro(2H-1-benzopyran-2,2'-indoline).

Spiro(indoline)naphthopyrans and spiro(indoline)quinopyrans may be represented by the following graphic formula VI,



wherein R_1 , R_2 , R_3 , R_4 and R_5 are as described with respect to

- 21 -

1 graphic formula III, R_6 and R_9 may each be selected from hydrogen,
 3 C_1-C_4 alkyl, C_1-C_4 alkoxy, nitro, and halogen, e.g., chloro fluoro or
 5 bromo, and Y is carbon or nitrogen.

Examples of spiro(indoline)naphthopyrans, include:

- 5 1,3,3-trimethyl spiro[indoline-2,2'-[2H]-naphtho[1,2-b] pyran];
 1,3,3,5,6-pentamethylspiro[indoline-2,2'-[2H]-naphtho[1,2-b] pyran];
 7 1,3,3-trimethyl-5-methoxyspiro[indoline-2,2'-[2H]-naphtho[1,2-b]
 pyran]; 1,3,3-trimethyl 6'-chlorospiro[indoline-2,2'-[2H]-
 9 naphtho[1,2-b]pyran]; and 1,3,3-trimethyl-6'-nitrospiro[indoline-
 2,2'-[2H]-naphtho[1,2-b] pyran].

11 Examples of spiro(indoline)quinopyrans include:

- Spiro[2H-indole-2,3'-3H]pyrano[3,2-f]quinoline; 1,3,3-trimethyl
 13 Spiro[2H-indole-2,3'-[3H]pyrano[3,2-f]quinoline; 1,3,3,5,6-
 pentamethyl Spiro[2H-indole-2,3'-[3H]pyrano[3,2-f]quinoline;
 15 1,3,5,6-tetramethyl-3-ethyl Spiro[2H-indole-2,3'-[3H]pyrano-
 [3,2-f]quinoline; 1,3,3-trimethyl-5-methoxy Spiro[2H-indole-
 17 2,3'-[3H]pyrano[3,2-f]quinoline; and 5-chloro-1,3,3,6'-tetramethyl
 spiro[2H-indole-2,3'-[3H]pyrano[3,2-f]-quinoline.

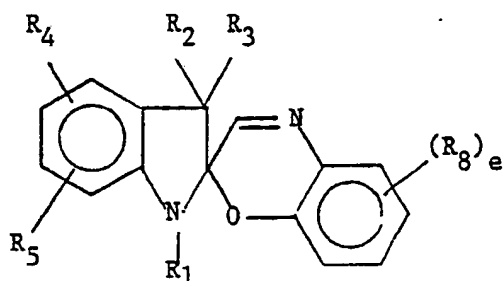
19 Spiro(indoline) benzoxazines may be represented by the
 following graphic formula VII.

21

23

25

27



(VII)

wherein R_1 , R_2 , R_3 , R_4 and R_5 are the same as described with respect
 29 to graphic formula III, and R_8 is selected from the group consisting
 of halogen, e.g., chloro, fluoro, or bromo, C_1-C_4 alkyl, e.g., C_1-C_2
 31 alkyl, C_1-C_5 alkoxy, e.g., C_1-C_2 alkoxy, nitro, cyano, thiocyno,
 C_1-C_4 monohaloalkyl, e.g., chloromethyl and chloroethyl, C_1-C_2

1 polyhaloalkyl, e.g., trihaloalkyl, such as trifluoromethyl and
2 1,1,1-trifluoroethyl, and mono-, di- or trialkylamino wherein the
3 alkyl moiety of the alkylamino group contains from 1 to 4 carbon
4 atoms, e.g., methylamino, dimethylamino, diethylamino, trimethylamino
5 and triethylamino. The letter "e" in formula VII is a number from 1
6 to 4, usually 1 to 3, more usually 1 to 2.

7 When "e" is 1, the R_g substituents may be located on any of
8 the available carbon atoms of the benzene ring of the benzoxazine
9 moiety, i.e., at the 5, 6, 7 or 8 positions. Preferably, the R_g
10 substituent is located on the 5, 6, or 7 carbon atoms. When "e" is 2
11 or more, the R_g substituents may be the same or different and in
12 either case are selected from the above-described group. When "e" is
13 2, the R_g substituents may be located at the 5 and 7 or 6 and 8
14 positions.

15 Examples of spiro(indoline)benzoxazines within the scope of
16 graphic formula VII are listed in Table III. Compound 1 may be
17 named: 7-methoxy-1',3',3',4'(and 6'), 5'-pentamethylspiro[2H-1,4-
18 benzoxazine-2,2'-indoline]. Compounds 2-48 may be similarly named as
19 substituted spiro(indoline) benzoxazines using the substituents
20 described in Table V for such compounds. In naming the
21 spiro(indoline)benzoxazines, the IUPAC rules of organic nomenclature
22 have been used. The positions on the indoline portion of the
23 molecule have been numbered counterclockwise starting with the
24 nitrogen atom as number one (1), and are identified by a prime
25 number, e.g., 3'. The positions on the benzoxazine portion of the
26 molecule have been numbered clockwise starting with the oxygen atom
27 as number one (1).

1

Table III

3

SUBSTITUENT

5	Compound		R ₁	R ₂	R ₃	R ₄	R ₅	R ₈	R ₈
	No.								
7	1		Me	Me	Me	4(6)-Me	5-Me	7-OMe	-
	2		Me	Me	Me	4(6)-Me	5-Me	7-OMe	5-OMe
9	3		Me	Me	Me	5-OMe	-	7-OMe	5-OMe
	4		Me	Me	Me	4(6)-Me	5-Me	7-OMe	5-Cl
11	5		Me	Me	Me	4(6)-Me	5-Me	6-NO ₂	-
	6		Me	Me	Me	4(6)-Me	5-Me	6-Cl	-
13	7		Me	Me	Ph	-	-	7-OMe	-
	8		Me	Me	Et	-	-	7-OMe	5-OMe
15	9		n-Bu	Me	Me	-	-	7-OMe	5-OMe
	10		Me	Cyclohexyl	-	-	-	7-OMe	5-OMe
17	11		Me	Me	Me	5-OMe	-	6-NO ₂	-
	12		Me	Me	Me	5-OMe	-	6-NO ₂	8-OMe
19	13		Et	Me	Me	5-OMe	-	6-NO ₂	8-OMe
	14		Me	Me	Et	4(6)-Me	5-Me	6-NO ₂	8-OMe
21	15		Me	Me	Ph	-	-	6-NO ₂	8-OMe
	16		Me	Me	Me	4(6)-Me	5-Me	8-NO ₂	6-OMe
23	17		Me	Me	Me	-	-	8-NO ₂	6-OMe
	18		Me	Me	Me	5-OMe	-	8-NO ₂	6-OMe
25	19		Et	Me	Me	-	-	7-OMe	6-Br
	20		Me	Me	Et	4(6)-Me	5-Me	7-OMe	5-Me
27	21		i-Pr	Me	Me	5-OMe	-	7-OMe	5-OMe
	22		Me	Me	Me	-	-	7-NEt ₂	-
29	23		Benzyl	Me	Me	-	-	7-NO ₂	-
	24		Me	Me	Me	4(6)-F	-	7-OMe	5-OMe
31	25		Me	Me	Me	6-Cl	-	7-OMe	5-OMe
	26		Me	Me	Me	7-F	-	7-OMe	5-OMe
33	27		Me	Me	Me	7-Cl	-	7-OMe	5-OMe
	28		Me	Me	Me	7-Br	-	7-OMe	5-OMe

1

Table III

3

SUBSTITUENT

Compound		R ₁	R ₂	R ₃	R ₄	R ₅	R ₈	R ₈
5	No.							
7								
	29	Me	Me	Me	5-F	-	7-OMe	5-OMe
9	30	Me	Me	Me	5-Cl	-	7-OMe	5-OMe
	31	Me	Me	Me	5-OMe	-	7-OMe	5-OMe
11	32	Me	Me	Me	5-OMe	-	7-OMe	-
	33	Me	Me	Me	6-CF ₃	-	7-OMe	5-OMe
13	34	Me	Me	Et	4(6)-F	-	7-OMe	5-OMe
	35	Me	Me	Me	4(6)AcO	-	7-OMe	5-OMe
15	36	Me	Me	Me	4(6)CF ₃	-	7-OMe	5-OMe
	37	Me	Me	Me	4(6)F	5-F	7-OMe	5-OMe
17	38	Me	Me	Me	4(6)Cl	5-Cl	7-OMe	5-OMe
	39	Me	Me	Me	4(6)F	-	7-OMe	5-Cl
19	40	Me	Me	Me	4(6)F	-	7-OMe	5-F
	41	Me	Me	Me	4(6)AcO	-	7-OMe	5-OMe
21	42	Me	Me	Me	-	5-AcO	7-OMe	5-OMe
	43	Me	Me	Me	4(6)AcO	5-F	7-OMe	5-OMe
23	44	Me	Me	Me	4(6)AcO	5-Cl	7-OMe	5-OMe
	45	CNPr	Me	Me	-	-	7-OMe	-
25	46	C(O)OEt	Me	Me	-	-	7-OMe	5-OMe
	47	(EtO) ₂ Me	Me	Me	-	-	7-OMe	-
27	48	HOEt	Me	Me	-	-	7-OMe	-

29 Key:

	Me = methyl	Ph = phenyl	Br = bromine
31	n-Bu = n-butyl	OMe = methoxy	Cl = chlorine
	Et = ethyl	NO ₂ = nitro	F = fluorine
33	i-Pr = isopropyl	NEt ₂ = diethylamino	AcO = acetoxy
	CNPr = γ cyanoisopropyl	C(O)OEt = β -carboxyethyl	HOEt = hydroxyethyl
35	(EtO) ₂ Me = CH ₃ OCH ₂ CH ₂ OCH ₂ CH ₂ -		

37

1 Spiro(indoline) benzoxazines may be synthesized by reaction
of the corresponding R₈-substituted nitroso-phenol compound with the
3 corresponding R₄-and/or R₅-substituted indoline (Fischer's base) or
indolium salt, e.g., the iodide salt, compound. The two precursor
5 materials are reacted in substantially stoichiometric amounts in a
suitable solvent, such as toluene or ethanol, containing a base, such
7 as triethylamine or piperidine, at temperatures of from about 40°C.
to about 120°C. or 140°C. until the reaction is completed.

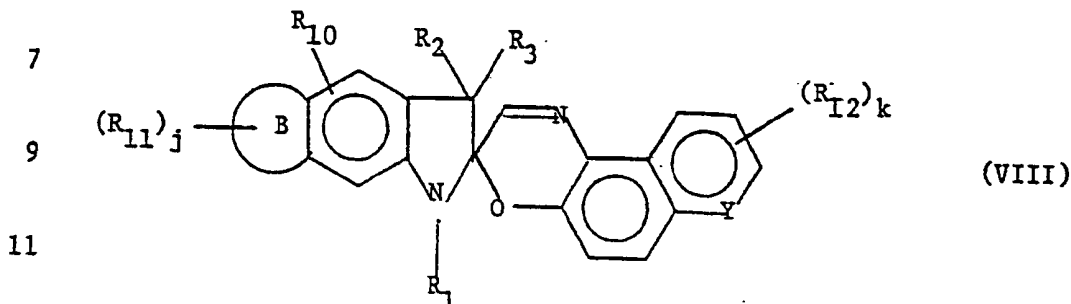
9 Any common organic solvent (polar and non-polar) except for
aliphatic hydrocarbon solvents, such as hexane, may be used as the
11 reaction medium. Suitable solvents include alcohols such as C₁-C₄
alkanols, e.g., methanol, ethanol, isopropanol, and the butanols;
13 aromatic solvents such as benzene, toluene and xylene; ketones such
as acetone, methyl ethyl ketone and methyl isobutyl ketone; esters
15 such as ethyl acetate; chlorinated lower aliphatic hydrocarbons such
as methylene chloride and chloroform; dimethylsulfoxide,
17 dimethylformamide and tetrahydrofuran.

While reaction temperatures below 40°C. may be used, the
19 reaction rate is very slow and commercially unacceptable. Reaction
temperatures above 120°C. may cause decomposition of the product.
21 Hence, temperatures of from 40°C. to 120°C., e.g., 50°C. to 100°C.
are contemplated. Stirring of the reaction medium at elevated
23 reaction temperatures within the aforesaid ranges is recommended to
prevent decomposition of the benzoxazine product.

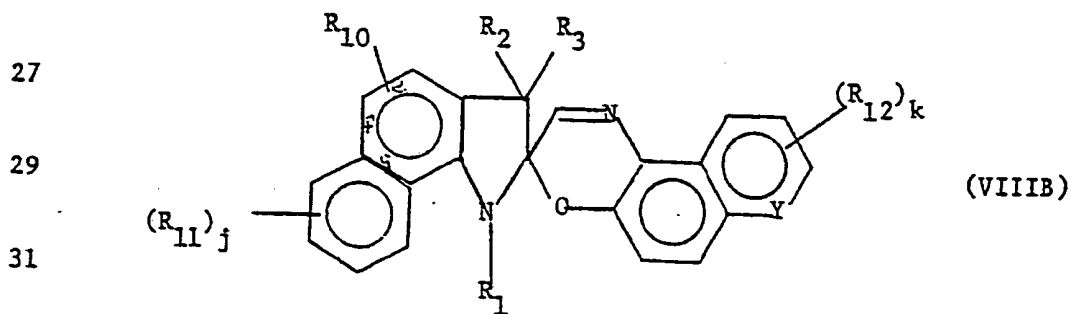
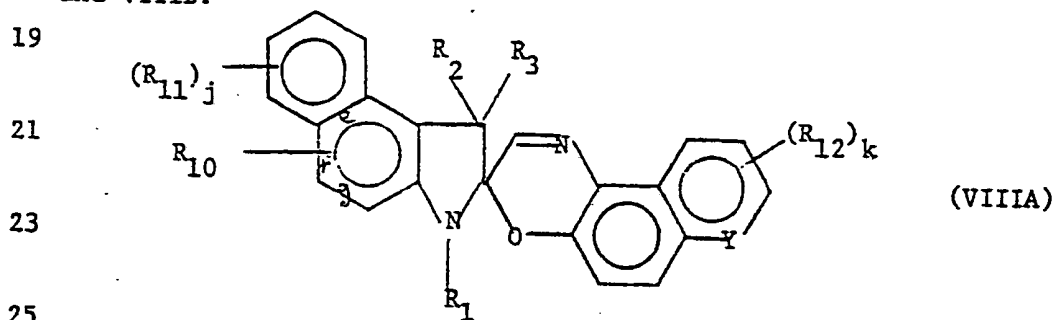
25 Any organic or inorganic base may be used to react with the
hydrogen halide that are liberated during the reaction as a result of
27 using the indolium halide salt. Amines such as trimethylamine,
triethylamine, diisopropylamine, piperidine, pyridine and piperazine
29 may be used. Inorganic basic reagents such as sodium carbonate,
sodium bicarbonate, potassium hydroxide, sodium hydroxide and sodium
31 acetate may be used. The use of inorganic reagents will entail a
two-phase reaction medium, i.e., an inorganic and organic phase. The
33 basic reagent is commonly used in a stoichiometric excess, although
stoichiometric amounts may be used.

1

3 Spiro(benzindoline) pyrido benzoxazine and
 5 spiro(benzindoline) naphthoxazine photochromic compounds may be
 7 represented by the following graphic formula VIII,



13 Ring B represents a substituted or unsubstituted benzene
 15 ring fused to the six membered ring of the indoline portion of the
 17 depicted formula. Ring B may be fused at the e, f, or g face of the
 indoline portion of the compound. Preferably, ring B is fused at the
 e or g face, as represented respectively by graphic formulae VIIIA
 and VIIIB:



33 In the above graphic formulae, Y is carbon or nitrogen, and R₁, R₂
 and R₃ are the same as described with respect to graphic formula III.

- 27 -

1 When Y is carbon and the R_{12} substituent(s) is other than
hydrogen, each R_{12} substituent in graphic formula VIII may be
3 selected from the group consisting of halogen, e.g., chloro, fluoro
or bromo, C_1-C_5 alkyl, C_1-C_5 alkoxy, e.g., methoxy, ethoxy, propoxy,
5 butoxy and pentoxy, nitro, cyano, thiocyno, C_1-C_4 monohaloalkyl,
e.g., C_1-C_4 monochloroalkyl such as chloromethyl and chloroethyl,
7 C_1-C_2 polyhaloalkyl, as for example trihaloalkyl such as trichloro-
or trifluoroalkyl, e.g., trifluoromethyl and 1,1,1-trifluoroethyl,
9 and mono- or dialkylamino wherein the alkyl moiety of the alkylamino
group contains from 1 to 4 carbon atoms, e.g., methylamino,
11 ethylamino, propylamino, dimethylamino and diethylamino. The letter
"k" in formula VIII is a number of from 0 to 2, e.g., 1 and denotes
13 the number of non-hydrogen substituents. In particular, each R_{12}
substituent may be selected from the group C_1-C_2 alkyl, C_1-C_2 alkoxy,
15 chloro, fluoro, bromo, nitro, and trifluoromethyl when e is 1 or 2.

 When Y is carbon and "k" is 1, the R_{12} substituent may be
17 located on any of the available carbon atoms of the naphtho moiety of
the naphthoxazine portion of the compound, i.e., at the 5', 6', 7',
19 8', 9' or 10' positions. Preferably, the R_{12} substituent is present
on the 7', 8' or 9' carbon atoms. When "k" is 2, the R_{12} substituents
21 may be the same or different and, in either case, are selected from
the above-described group. When "k" is 2, the R_{12} substituents are
23 commonly located at the 7' and 9' or 8' and 10' positions.

 When Y is nitrogen and the R_{12} substituent(s) is other than
25 hydrogen, each R_{12} substituent may be selected from C_1-C_5 alkyl,
e.g., C_1-C_2 alkyl, C_1-C_5 alkoxy, e.g., C_1-C_2 alkoxy, and halogen,
27 e.g., chloro, fluoro or bromo. Typically, k is 0 (zero) when Y is
nitrogen and thus there are no non-hydrogen substituents. When "k"
29 is 1 and Y is nitrogen, the R_{12} substituent may be located on any of
the available carbon atoms of the pyridobenz moiety of the
31 pyridobenzoxazine portion of the compound, i.e., at the 5', 6', 8',
9' or 10' positions, more usually at the 8', 9' or 10' positions.

1 When "k" is 2, the R_{12} substituent may be the same or different and,
in either case, are selected from the above-described group and are
3 located at two of aforescribed available carbon atoms.

R_{10} in graphic formula VIII is selected from the group
5 consisting of hydrogen, halogen, e.g., chloro, fluoro or bromo, C_1-C_5
alkyl, e.g., C_1-C_2 alkyl, C_1-C_5 alkoxy, e.g., C_1-C_2 alkoxy, C_1-C_4
7 monohaloalkyl, e.g., C_1-C_2 monohaloalkyl such as chloromethyl,
chloroethyl and fluoromethyl, C_1-C_2 polyhaloalkyl, as for example
9 trihaloalkyl such as trichloro- or trifluoro-alkyl, e.g.,
trifluoromethyl, cyano and C_1-C_8 alkoxycarbonyl. The R_{10} substituent
11 may be located at either the number 4 or 5 carbon atom positions.

R_{11} in graphic formula VIII is selected from the group
13 consisting of halogen, e.g., chloro, fluoro or bromo, C_1-C_5 alkyl,
e.g., C_1-C_2 alkyl, C_1-C_5 alkoxy, e.g., C_1-C_2 alkoxy, cyano, C_1-C_8
15 alkoxycarbonyl, C_1-C_2 polyhaloalkyl, C_1-C_4 monohaloalkyl and mono- or
di-alkylamino wherein the alkyl moiety of the alkylamino group
17 contains from 1 to 4 carbon atoms, e.g., methylamino, ethylamino,
propylamino and diethylamino.

19 The letter "j" in formula VIII is a number of from 0 to 2,
e.g., 0 or 1, more typically 0. When there are substituents on the
21 benz moiety of the benzindoline portion of the compound and the
letter "j" is 1 or 2, it denotes the number of non-hydrogen
23 substituents. When "j" is 1, the R_{11} substituent may be located at
the number 6, 7 or 8 carbon atoms. Similarly, when "j" is 2, the R_{11}
25 substituents may be present at the 6 and 7, 6 and 8, or 7 and 8
carbon atoms.

27 Of particular interest, are photochromic materials
represented by graphic formulae VIIIA and VIIIB wherein Y is N; R_1 is
29 a C_1-C_4 alkyl, such as methyl, ethyl, n-propyl, isopropyl, n-butyl,
secondary butyl, isobutyl and tertiary butyl; R_2 and R_3 are each
31 methyl, ethyl or phenyl; R_{12} is selected from C_1-C_4 alkyl, C_1-C_4
alkoxy, chloro, fluoro or cyano; R_{10} is selected from hydrogen,
33 fluoro, trifluoromethyl and C_1-C_4 alkyl; R_{11} is selected from C_1-C_4
alkyl, C_1-C_4 alkoxy, chloro, fluoro and C_1-C_4 mono- or di-alkylamino;
35 "j" is 0 or 1; and "k" is 0 or 1.

1 Examples of spiro(benzinoline)-type compounds within the
scope of graphic formulae VIII are listed in Tables IV and V. In
3 Table IV, Y is carbon. In Table V, Y is nitrogen. Compound 1 of
Table IV may be named: 9'-methoxy-1,3,3-trimethylspiro [benz[e]
5 indoline-2,3'[3H] naphth [2,1-b][1,4] oxazine]. Usually, the R₁₂
substituent (when "k" is 1) will be located at the 8' or 9' carbon
7 atom, more usually at the 9' carbon atom. When 'k' is 2 and Y is
carbon, the R₁₂ substituents will usually be located at the 7' and 9'
9 carbon atoms. For example, in Table IV, the recited methoxy (OMe)
and ethoxy (OEt) substituents will commonly be a 9'-methoxy or
11 9'-ethoxy substituent. The dimethoxy substituents of compound 13
will commonly be 7', 9'-dimethoxy substituents. The bromo
13 substituent of compound 25 may be an 8'-bromo substituent. Compounds
in Tables IV and V may be similarly named as substituted spiro
15 benz(indoline) naphthoxazines or spiro benz(indoline) pyrido
benzoxazines using the substituents described in the Tables for such
17 compounds. In naming compounds herein, the IUPAC rules of organic
nomenclature have been used.

1

Table IV

SUBSTITUENT (Y = C)

3 Compound		SUBSTITUENT (Y = C)						Face
5 No.		R ₁	R ₂	R ₃	R ₁₂	R ₁₀	R ₁₁	
7								
9	1	Me	Me	Me	OMe	H	-	e
	2	Me	Me	Me	OMe	H	-	g
	3	Et	Me	Me	OMe	H	-	e
11	4	n-Pr	Me	Me	OMe	H	-	e
	5	i-Pr	Me	Me	OMe	H	-	e
13	6	Et	Me	Me	OMe	H	-	g
	7	n-Pr	Me	Me	OMe	H	-	g
15	8	Me	Me	Me	OMe	F	-	e
	9	Me	Me	Me	OMe	CF ₃	-	e
17	10	Me	Me	Me	OMe	F	-	g
	11	Me	Me	Me	OMe	CF ₃	-	g
19	12	Me	Me	Ph	OMe	H	Cl	g
	13	Me	Me	Me	(OMe) ₂	OMe	-	g
21	14	Et	Me	Me	NEt ₂	H	OMe	e
	15	Me	Me	Me	OMe	Me	Me	g
23	16	Me	Me	Me	Me	Me	Me	e
	17	Me	Me	Me	NO ₂	CF ₃	-	g
25	18	Me	Me	Me	Cl	H	-	e
	19	i-Pr	Me	Me	CF ₃	H	-	e
27	20	Me	Me	Me	ClMe	CF ₃	-	g
	21	Me	Me	Me	OMe	AcO	-	g
29	22	Me	Me	Me	OMe	ClMe	Cl	e
	23	Me	Me	Me	-	H	-	e or g

1

TABLE IV (continued)

3	Compound							Face
	No.	R ₁	R ₂	R ₃	R ₁₂	R ₁₀	R ₁₁	
5	24	Me	Me	Me	OEt	H	-	e or g
7	25	Me	Me	Me	Br	H	-	e or g
	26	(CH ₂) ₃ CN	Me	Me	OMe	H	-	e or g
9	27	(CH ₂)COOH	Me	Me	OMe	H	-	e or g
	28	(CH ₂) ₂ OH	Me	Me	OMe	H	-	e or g

1

Table V

SUBSTITUENT (Y = N)

3 Compound		SUBSTITUENT (Y = N)						Face
No.		R ₁	R ₂	R ₃	R ₁₂	R ₁₀	R ₁₁	
5								
7	1	Me	Me	Me	H	H	-	e
	2	Me	Me	Me	H	H	-	g
9	3	Me	Me	Me	Me	H	-	e or g
	4	Me	Me	Me	OMe	H	-	e or g
11	5	Me	Me	Me	Cl	H	-	e or g
	6	Me	Me	Me	-	F	-	e or g
13	7	Me	Me	Me	-	CF ₃	-	e or g
	8	Et	Me	Me	-	H	-	e or g
15	9	n-Pr	Me	Me	-	H	-	e or g
	10	i-Pr	Me	Me	-	H	-	e
17	11	Me	Me	Et	Me	CF ₃	F	g
	12	Me	Me	Me	OMe	Me	Me	g
19	13	Me	Me	Et	OMe	H	OMe	g
	14	Me	Me	Me	OMe	F	NEt ₂	g
21	15	Me	Me	Et	F	F	Me	g
	16	Me	Me	Me	Me	H	-	e or g
23	17	(CH ₂) ₃ CN	Me	Me	-	H	-	e or g
	18	(CH ₂) ₂ COOH	Me	Me	-	H	-	e or g
25	19	(CH ₂) ₂ OH	Me	Me	-	H	-	e or g
	20	Me	Me	Me	-	H	CF ₃	e or g
27	21	Me	Me	Me	-	H	F	e or g

1 Key For Tables:

- Me = methyl
- 3 Ph = phenyl CF₃ = trifluoromethyl
- Et = ethyl OMe = methoxy ClMe = chloromethyl
- 5 n-Pr = n-propyl NO₂ = nitro Cl = chlorine
- i-Pr = isopropyl NEt₂ = diethylamino F = fluorine
- 7 (CH₂)₃CN = cyanopropyl (CH₂)₂OH = hydroxyethyl AcO = acetoxy
- (CH₂)₂COOH = carboxyethyl
- 9 A hyphen (-) denotes the absence of non-hydrogen substituents

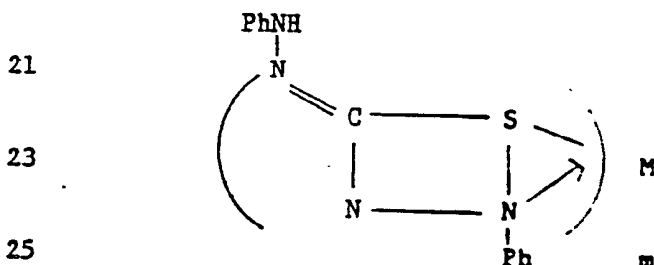
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3 The photochromic materials of the present invention may be
 synthesized by reaction of the corresponding R_{10} and $(R_{11})_j$ -
 5 substituted indoline (Fischer's base) or indolium salt, e.g., the
 iodide salt, with the corresponding $(R_{12})_k$ -substituted-1-nitroso-
 7 2-naphthol or $(R_{12})_k$ -substituted-5-nitroso-6-quinolinol.

The two precursor materials are reacted in substantially
 9 stoichiometric amounts in a suitable solvent, such as toluene or
 ethanol, containing a base, such as triethylamine or piperidine,
 11 (when the indolium salt is used) at temperatures of from about 40°C.
 to about 140°C., more usually from 40°C. to 120°C., until the
 13 reaction is completed.

Photochromic organometal dithizonates, i.e., (arylaazo)
 15 thioformic arylhydrazidates, may be used as the photochromic
 substance to prepare the photochromic pigment described herein.
 17 Typically, such substances are mercury dithizonates, but may be
 represented by the following graphic formula:

19

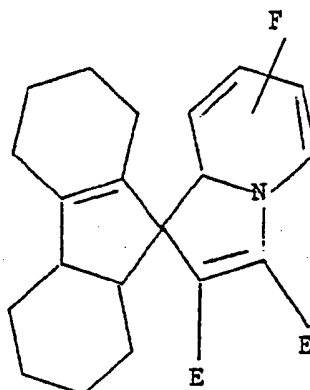


27 wherein M is mercury, palladium, platinum, nickel, silver, zinc,
 cadmium, bismuth and lead, m is a whole positive integer of from 1 to
 29 3, e.g., 2, and Ph is phenyl or methyl substituted phenyl.

Preferably M is mercury. See, for example, U.S. Patent 3,361,706.

1 Examples of some common mercury dithizonates are:
 mercury bis (diphenylthiocarbazonate), diphenylthiocarbazonomercuric
 3 chloride, fluoride, iodide or bromide, dinaphthylthiocarbazono-
 mercuric chloride, fluoride, iodide or bromide, ditolylthio-
 5 carbazonomercuric chloride or fluoride, mercury bis(dinaphthylthio-
 carbazonate), mercury bis(ditolylthiocarbazonate), ethylmercuric
 7 diphenylthiocarbazonate and phenylmercuric diphenylthiocarbazonate.

 Spirodihydroindolizines are another known group of
 9 photochromic substances that have recently been developed by H.
 Durr. These substances may be represented by the following graphic
 11 formula:

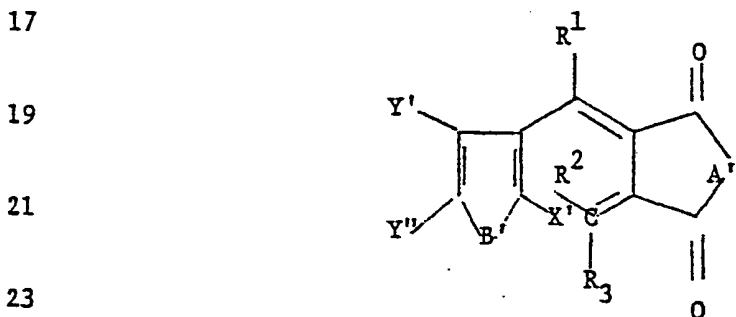


21 wherein E is hydrogen, C(O)R, OC(O)R, CN, or CF₃ wherein R is
 a C₁-C₄ alkyl, and F may be a C₁-C₄ alkyl, C₁-C₄ alkoxy, di(C₁-C₂)
 23 alkylamino, cyano, phenyl and C(O)R. See, for example, Germany
 Patents DE 3,320,077, 3,220,257 and 2,906,193, which are incorporated
 25 herein by reference. Examples of such spirodihydroindolizines are:
 2,3-Dicarbomethoxy-8a-methyl-spiro [1,5,6,8a-tetra-hydropyrrolo-
 27 [1,2-a]- [3,4]-dihydroisoquinoline-1,9'-fluorene], 2,3-dicarbo-
 methoxy-8a-phenyl-spiro [1,5,6,8a-tetra-hydropyrrolo-[1,2-a]-
 29 [3,4]-dihydroisoquinoline-1,9'-fluorene] 2,3-dicarbomethoxy-
 8a-thiophene-9,10-dimethoxy-spiro[1,5,6,8a-tetrahydro-
 31 pyrrolo-[1,2-a]-[3,4]-dihydroisoquinoline-1,9'-fluorene],
 2,3-dicyano-8a-phenyl-spiro[1,5,6,8a-tetrahydro-pyrrolo-[1,2-a]-[3,4]-
 33 dihydroisoquinoline-1,9'-fluorene],

1 2,3-dicyano-8a-methyl-spiro[1,5,6,8a-tetrahydro-pyrrolo-[1,2-a]-[3,4]-
 dihydroisoquinoline-1,9'-fluorene], 2,3-dicarbomethoxy-spiro-
 3 [1,2,3,8a-tetrahydropyrrolo-[1,2-a]-isoquinoline- 1,9'-fluorene],
 2,3-dicarbomethoxy-spiro[1,7,8,8a-tetrahydropyrrolo-[1,2-a]-[3,4]-di-
 5 hydroquinoline-1,9'-fluorene], and 2,3-dicarbomethoxy-spiro
 [1,7,8,8a-tetrahydropyrrolo-[2,1-f]-[4,5]-di-hydropyridazine-1,9'-
 7 fluorene].

The fulgides and fulgimides represent a further group of
 9 photochromic compounds that may be used to prepare the organic
 photochromic pigment of the present invention. Examples include the
 11 3-furyl and 3-thienyl fulgides and fulgimides described in U.S. patent
 4,220,708, and the 3-pyrryl fulgides and fulgimides described in British
 13 Patent Application 2,170,202. Such patents are incorporated herein by
 reference.

15 Photochromic heterocyclic fulgides and fulgimides of U.S.
 4,220,708 are represented by the following graphic formula,



(IX)

wherein R^1 represents a C_1 - C_4 alkyl, phenyl, mono- and di(C_1 - C_4) alkyl
 25 substituted phenyl, e.g., tolyl, or phen (C_1 - C_4) alkyl, e.g., benzyl
 group; A' represents oxygen or $=N-R^4$, in which R^4 is C_1 - C_4 alkyl or
 27 phenyl, B represents oxygen or sulfur, R^2 and R^3 independently represent
 a C_1 - C_4 alkyl, phenyl or phen(C_1 - C_4) alkyl or one of R^2 and R^3 is
 29 hydrogen and the other is one of the aforementioned groups, or $R^2R^3C=$
 represents an adamantylidene group, X' represents hydrogen or R^1 and Y'
 31 and Y'' are each selected from hydrogen, halogen, e.g., chloro, fluoro,
 bromo or iodo, R^1 , C_1 - C_4 alkoxy, e.g., methoxy, and phenoxy. Examples of

- 37 -

- 1 such compounds include: (Z)- α -2,5-dimethyl-3-furylethylidene
 (isopropylidene) succinic anhydride,
 3 (Z)- α -2-benzyl-3-benzfurylethylidene (isopropylidene) succinic
 anhydride, (Z)- α -2,5-dimethyl-3-thienylethylidene (isopropylidene)
 5 succinic anhydride, (E)- α -2-methyl-3-furylethylidene-(isopropylidene)
 succinic anhydride, (Z)- α -2,5-diphenyl-3-furylethylidene(isopropylidene)
 7 succinic anhydride,
 2,5-dimethyl-3-furyl(3',5'-dimethoxyphenyl)methylene-E-benzylidene
 9 succinic anhydride, and adamant-2-ylidene-(2',5'-dimethyl-3'furyl)
 ethylidene succinic anhydride.

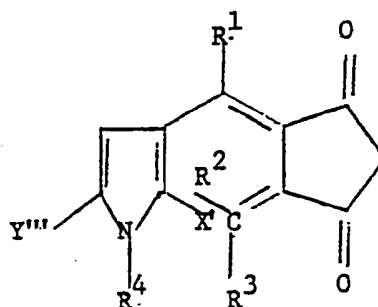
11 Photochromic heterocyclic fulgides and fulgimides of British
 Patent 2,170,202 may be represented by the following graphic formula,

13

15

17

19



(X)

wherein R^1 , R^2 , R^3 and X' are described with respect to formula IX,
 21 $R^4=R^1$, and Y''' is a C_1 - C_4 alkyl phenyl, or phen (C_1 - C_4) alkyl group.
 Examples of compounds represented by formula X include:

- 23 (E)- α -(1,2,5-trimethyl-3-pyrrolyl)ethylidene (isopropylidene) succinic
 anhydride,
 25 (E)- α -(2,5-dimethyl-1-phenyl-3-pyrrolyl) ethylidene (isopropylidene)
 succinic anhydride,
 27 (E)- α -(2,5-dimethyl-1-p-tolyl-3-pyrrolyl) ethylidene (isopropylidene)
 succinic anhydride,
 29 (E)- α -(1,5-diphenyl-2-methyl-3-pyrrolyl) ethylidene (isopropylidene)
 succinic anhydride, and
 31 (E)- α -(2,5-dimethyl-1-phenyl-3-pyrrolyl) ethylidene
 (dicyclopropylmethylene) succinic anhydride.

33 The organic photochromic pigment prepared in accordance with
 the present invention is a fine powder which may be incorporated into any
 35 suitable vehicle that is transparent to ultraviolet light or used in any

1 application where pigmentary materials are utilized. For example, the
aforesaid pigment can be incorporated into paints, inks, coating
3 compositions, adhesives and admixed with other polymeric materials and
formed into various shapes by, for example, casting and injection
5 molding. The host (carrier) in which the pigment is housed must be
transparent to visible light including ultraviolet light to allow
7 activation of the pigment. The photochromic pigment may be used also as
an additive to polymerizable monomeric compositions, which when
9 polymerized produce a polymerizate containing a homogenous dispersion of
the pigment throughout the polymer.

11 The present process is more particularly described in the
following examples which are intended as illustrative only, since
13 numerous modifications and variations therein will be apparent to those
skilled in the art.

15

Example 1

17 Twenty grams of ethylene glycol dimethacrylate and 0.01 grams
of 1,3,3,4,5 (and 5,6) pentamethyl spiro[indoline]-2,3'[3H]pyrido [3,2-f]
19 [1,4] benzoxazine] were charged to a tared 50 milliliter (ml) beaker.
The mixture was stirred to dissolve the spiro(indoline)pyridobenzoxazine
21 and 0.108 parts (per hundred parts of monomer) of diisopropyl
peroxydicarbonate added to the mixture, which was stirred and poured into
23 a 4 inch x 4 inch x 1/16 inch (10.16 cm x 10.16 cm x 0.16 cm) sheet
mold. After standing at room temperature overnight, the mold was place
25 in a recirculating air oven maintained at 45°C. The mold was maintained
at that temperature for 4 hours. Thereafter the oven temperature was
27 increased to 50°C. and the mold maintained at that temperature for 18
hours. The resulting sheet was demolded. The sheet cracked during the
29 demolding procedure. A portion of the cast sheet was ground into a fine
powder using a mortar and pestle. Both the cast sheet and pigment powder
31 exhibited a color change, i.e., a photochromic effect, when exposed to
ultraviolet light.

- 39 -

1 The above procedure was repeated, except that the photochromic
substance used was 1,3,3-trimethyl-5-methoxy-spiro[indoline]-
3 2,3'[3H]pyrido [3,2-f] [1,4] benzoxazine]. Similar results were obtained.

5 Example 2

The procedure of Example 1 was repeated, except that 0.04 grams
7 of 5,7-dimethoxy-1',3',3',4'(and 6'), 5'-pentamethylspiro[2H-1,4-
benzoxazine-2,2'-indoline] was used as photochromic substance. Results
9 similar to that obtained in Example 1 were observed.

EXAMPLE 3

11 A tared 250 ml. beaker was charged with 115 grams of hexane
diol diacrylate, 0.12 grams of the photochromic substance of Example 1,
13 and 0.115 grams of diisopropyl peroxydicarbonate, and the mixture stirred
for several minutes. 102.5 grams of the resultant reaction mixture was
15 transferred to a 28 oz. Boston round bottle containing 300 ml. of an
aqueous polymerization medium prepared by mixing 754.5 grams of distilled
17 water, 3.7 grams of Acrysol® ASE-95 polyacrylic acid, 5.0 grams of sodium
bicarbonate and 0.19 grams of sodium hydroxide. The bottle was purged
19 with argon for about 3 to 4 minutes, sealed, shaken vigorously and placed
in a 45°C. temperature tumbling water bath for 18 hours. A pinkish
21 polymer was recovered from the polymerization bottle by filtration,
washed with distilled water and dried under vacuum at 40°C. for 18
23 hours. The resulting dried polymer powder was photochromic, i.e., it
changed to a blue color when irradiated with ultraviolet light. The
25 ultimate particle size of the powder appeared to be about 5/3 micrometers
with the powder comprising agglomerates of 18-25 micrometers. A portion
27 of the powder product was ground gently with a mortar and pestle to
break-up the agglomerates and a portion of this ground product further
29 ground in an oscillating grinder for 30 seconds three times, i.e., a
total of 90 seconds grinding time. This powder was spread on a glass
31 plate and exposed to ultraviolet light. It remained photochromic.

- 40 -

1

EXAMPLE 4

The general procedure of Example 3 was used to prepare a photochromic polymer of ethylene glycol dimethacrylate. 100 grams of the monomer was mixed with 0.2 grams of the photochromic substance of Example 1 and 0.25 grams (0.05 phm) of diisopropyl peroxydicarbonate. The resultant mixture was added to 300 ml of an aqueous polymerization medium prepared from 765 grams of distilled water, 3.83 grams of sodium lauryl sulfate, 9.56 grams of Acrysol® ASE-95 polyacrylic acid, 3.06 grams of sodium bicarbonate and 0.55 grams of sodium hydroxide. Polymerization was conducted overnight at 45°C. The polymer product was recovered by filtration, the filter cake broken-up with a mortar and pestle, this ground product washed with methanol and dried to a free flowing powder. The dried powder was photochromic. 25 grams of the dried powder was ground in an oscillating grinder for 1 minute. The average particle size was found to be about 23 micrometers. After grinding for 12 hours in a ball mill, the average particle size had been reduced to 8 micrometers.

17

EXAMPLE 5

A polymerizable mixture was prepared by combining 334.61 grams of diethylene glycol dimethacrylate, 165.39 grams of trimethylol propane trimethacrylate, 2.50 grams of the photochromic substance of Example 1 and 0.497 grams of diisopropyl peroxydicarbonate. Three 12 inch x 12 inch x 1/16 inch (30.5 cm x 30.5 cm x .16 cm) molds were filled with the mixture; the filled molds were left overnight at room temperature and then placed in an oven for 16 hours at 45°C. Thereafter, the oven temperature was increased to 100°C. over 3 hours and maintained at 100°C. for 1 hour. The cured sheets were allowed to cool and then removed from the molds. The polymer sheets fractured on cooling. The fractured sheets were broken into smaller pieces and ball milled to an average particle size of 0.6 micrometers. The resultant powder product was photochromic.

While the above invention has been illustrated, particularly with spiro(indoline)-type photochromic substances, it expected that similar results will be obtained by substituting other photochromic

- 41 -

1 materials. Similarly the use of polyfunctional acrylate monomers other
2 than those specifically described in the examples are expected to provide
3 similar results.

4 Although the present invention has been described with
5 reference to the specific details of certain embodiments thereof, it is
6 not intended that such detail should be regarded as limitations upon the
7 scope of the invention, except as and to the extent that they are
8 included in the accompanying claims.

1

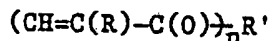
CLAIMS

3 1. Photochromic particulate thermoset resin having an average
particle diameter between about 0.25 and 20 micrometers and having a
5 photochromic amount of an organic photochromic substance uniformly
dispersed throughout the particulate resin, said thermoset resin being a
7 polymerizate of a polyfunctional acrylate monomer composition which is
polymerized in the presence of said photochromic substance.

9

2. The particulate thermoset resin of claim 1 wherein the
11 polyfunctional acrylate monomer composition includes at least one
acrylate monomer represented by the following formula,

13



15

wherein R is hydrogen or methyl, n is the number 2, 3 or 4 and R' is the
17 multivalent radical remaining after removal of the hydroxy groups from a
polyol having from 2 to 4 hydroxy groups.

19

3. The particulate thermoset resin of claim 2 wherein R' is
21 selected from C₂-C₈ glycols, cyclohexane diol, diethylene glycol,
triethylene glycol, tetraethylene glycol, dipropylene glycol, C₂-C₅
23 triols and pentaerythritol, and n is 2 or 3.

25

4. The particulate thermoset resin of claim 3 wherein the
organic photochromic substance is selected from the group consisting of
27 spiro(indoline)-type compounds, metal dithizonate compounds, fulgides,
fulgimides, and spirodihydroindolizines.

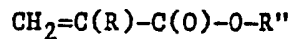
29

5. The particulate thermoset resin of claim 4 wherein the
31 spiro(indoline)-type compounds are selected from the group consisting of
spiro(indoline) pyrido benzoxazines, spiro(indoline) naphthoxazines,
33 spiro(benzindoline) pyrido benzoxazines, spiro(benzind line)

1 naphthoxazines, spiro(indoline) benzopyrans, spiro(indoline
naphthopyrans, spiro(indoline) quinopyrans, spiro(indoline) benzoxazines
3 and mixtures of such spiro(indoline) compounds.

5 6. The particulate thermoset resin of claim 2 wherein the
polyfunctional acrylate monomer composition contains from about 1 to
7 about 20 weight percent of monofunctional copolymerizable monomer
selected from monofunctional acrylic and methacrylic esters and vinyl
9 esters of C₂-C₅ carboxylic acids.

11 7. The particulate thermoset resin of claim 6 wherein the
monofunctional acrylic esters are represented by the formula,
13

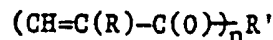


15
wherein R is hydrogen or methyl and R'' is selected from the group
17 consisting of C₁-C₁₂ alkyl, C₅-C₆ cycloalkyl, glycidyl and hydroxyethyl.

19 8. The particulate thermoset resin of claim 4 wherein from
about 0.01 to about 10 weight percent of the photochromic substance is
21 present in the particulate resin.

23 9. A method for producing a photochromic particulate
thermoset resin, which comprises dispersing a substantially uniform
25 mixture of polyfunctional acrylate monomer composition and a photochromic
amount of organic photochromic substance that is compatible with said
27 monomer in an aqueous polymerization medium, polymerizing the monomer,
and separating finely-divided thermoset photochromic particles from the
29 polymerization medium.

31 10. The method of claim 9 wherein the polyfunctional acrylate
monomer is represented by the following formula,
33



1 wherein R is hydrogen or methyl, n is the number 2, 3 or 4 and R' is the
multivalent radical remaining after removal of the hydroxy groups from a
3 polyol having from 2 to 4 hydroxy groups.

5 11. The method of claim 10 wherein R' is selected from C₂-C₈
glycols, cyclohexane diol, diethylene glycol, triethylene glycol,
7 tetraethylene glycol, dipropylene glycol, C₂-C₅ triols and
pentaerythritol, and n is 2 or 3.

9 12. The method of claim 11 wherein the polyfunctional monomer
11 polymerized contains from about 1 to about 20 weight percent of
monofunctional copolymerizable monomer selected from monofunctional
13 acrylic and methacrylic esters and vinyl esters of C₂-C₅ carboxylic acids.

15 13. The method of claim 12 wherein the monofunctional acrylic
esters are represented by the formula,



19 wherein R is hydrogen or methyl and R'' is selected from the group
consisting of C₁-C₁₂ alkyl, C₅-C₆ cycloalkyl, glycidyl and hydroxyethyl.
21

23 14. The method of claim 9 wherein the organic photochromic
substance is selected from the group consisting of spiro(indoline)-type
compounds, metal dithizonate compounds, fulgides, fulgimides, and
25 spirodihydroindolizines.

27 15. The method of claim 14 wherein the spiro(indoline)-type
compounds are selected from the group consisting of spiro(indoline)
29 pyrido benzoxazines, spiro(indoline) naphthoxazines, spiro(benzindoline)
pyrido benzoxazines, spiro(benzindoline) naphthoxazines, spiro(indoline)
31 benzopyrans, spiro(indoline naphthopyrans, spiro(indoline) quinopyrans,
spiro(indoline) benzoxazines and mixtures of such spiro(indoline)
33 compounds.

1 16. The method of claim 15 wherein the mixture of
polyfunctional acrylate monomer and photochromic substance contains from
3 0.01 to 10 weight percent of the photochromic substance.

5 17. The method of claim 16 wherein polymerization of the
monomer is by emulsion polymerization.

7
 18. The method of claim 9 wherein the finely-divided thermoset
9 photochromic particles separated from the polymerization medium are
milled to produce a product with average particle size reduced from that
11 originally obtained.

13 19. A method for producing a photochromic particulate
thermoset resin which comprises bulk polymerizing a substantially uniform
15 mixture of polyfunctional acrylate monomer composition and a photochromic
amount of organic photochromic substance that is compatible with said
17 monomer, thereby to produce a relatively brittle polymerizate and
subjecting the resulting polymerizate to attrition milling thereby to
19 produce finely-divided thermoset photochromic particulate resin.

21 20. The method of claim 19 wherein the polyfunctional
acrylate monomer is represented by the following formula,

23 $(CH=C(R)-C(O)\text{---}R')_n$

25 wherein R is hydrogen or methyl, n is the number 2, 3 or 4 and R' is the
multivalent radical remaining after removal of the hydroxy groups from a
27 polyol having from 2 to 4 hydroxy groups.

29 21. The method of claim 20 wherein R' is selected from C₂-C₈
glycols, cyclohexane diol, diethylene glycol, triethylene glycol,
31 tetraethylene glycol, dipropylene glycol, C₂-C₅ triols and
pentaerythritol, and n is 2 or 3.

33

1 22. The method of Claim 21 wherein the organic photochromic
substance is selected from the group consisting of spiro(indoline)-type
3 compounds, metal dithizonate compounds, fulgides, fulgimides, and
spirodihydroindolizines.

5

 23. The method of claim 22 wherein from 0.01 to about 10
7 weight percent of the photochromic substance is mixed with the
polyfunctional acrylate monomer composition.

9

 24. The method of claim 23 wherein the polymerizate is milled
11 to produce particulate photochromic resin having an average particle size
of between 0.25 and 20 micrometers.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 88 / 04176

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC (4): G 02 B 5/23; C08J 3/00

II. FIELDS SEARCHED

Minimum Documentation Searched ⁷

Classification System

Classification Symbols

US

252/586, 582

524/83

84

89

90

92

94

95

98

715

719

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched ⁸

III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	US, A, 3,578,602 (Ono et al) 11 May 1971 See the abstract, Column 2, and the claims.	1-24
Y	US, A, 4,342,668 (Hovey et al) 3 August 1982 See column 2 and the claims.	1-24
Y	US, A, 4,405,733 (Williams et al) 9 September 1983 See the entire document	1-24
Y	US, A, 4,166,043 (Uhlmann) 28 August 1979 See Column 1, lines 57-64, Column 2 Column 5, lines 49-5 and the Examples	1-24
Y	US, A, 4,132,561 (Burke Jr.) 10 January 1979 See entire document	1-24
Y	US, A, 4,503,177 (Reid) 15 March 1985 See entire document	1-24

¹⁰ Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"Z" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

20 February 1989

Date of Mailing of this International Search Report

10 APR 1989

International Searching Authority

ISA/US

Signature of Authorized Officer

Richard Treanor

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
Y	EP, A 227,337 (Maltman) 1 June 1987 See Example 1 and the claims	1-24
Y	JA, B 62-11743 (Sakagmi et al) 20 January 1987	1-24